Introductory Chemical Engineering Thermodynamics

Unit I. Earth, Air, Fire, and Water

Chapter 2: Energy Balances

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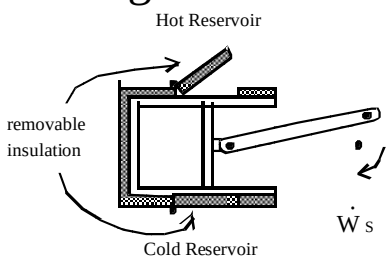
EC Work, Net Work, "Lost Work," Gradients, and Viscous Dissipation

Consider a piston+cylinder engine. Work energy leaves the system when the piston ***expands*** and work energy enters the system when the system ***contracts*** as a result of cooling. The ***net work*** transferred out of the system is the expansion-contraction work.



Heat enters instantly when the gas is fully ***contracted*** then ***expansion*** pushes a rod connected to a shaft that turns a wheel, then the gas is cooled and ***contracts*** to the original state. If all the work energy goes into the shaft, expansion or contraction is:

$$W_{EC} = -\int F\,dx = -\int F/A\,d(Ax) = -\int P\,dV$$

Where else could the work energy go besides the shaft?

ANS. Into friction if the piston is not lubricated or into stirring the gas in any real system. We will refer to the energy diverted from useful work by friction etc. as "***lost work***." Note: it's not really "lost." We know where it went, but it didn't go where we wanted.

Friction and stirring are really two sides of the same coin. In friction, two solid surfaces with nonzero relative velocities are rubbing together, disturbing and exciting the surface molecules and enhancing their velocities. In stirring, two ***viscous*** fluid planes with nonzero relative velocities are rubbing together, disturbing and exciting the molecules that are colliding across the fluid plane. In both these mechanisms, the nonzero relative ***velocity gradients*** lead to the energy being ***dissipated*** as a low grade temperature increase.

Pressure gradients, Maximal Work, and Reversibility

How can we minimize lost work?

ANS. By minimizing gradients. For instance, the velocity gradients of stirring could be reduced by expanding the gas slowly. But ***pressure gradients*** should also be minimized.

To see this, suppose the piston+cylinder was oriented in a vertical direction, and the cylinder was infinitely long, but there was no rod or shaft. Suppose the piston weighs 50g and a 1000g weight sits on top of it. If we knock the weight off, the gas will expand rapidly, giving kinetic energy to the piston. When the pressure in the cylinder equals atmospheric pressure the expansion should stop, but now the piston's kinetic energy takes over to generate a vacuum till the vacuum work brings the kinetic energy to zero. Then we go the other way, oscillating until the work of stirring damps the motion.

Next suppose that we define useful work as elevating some weight to some new height. Zero useful work is accomplished by the above process. Suppose we divide the weight in two, and only knock off half the weight. Then half the weight is elevated so some useful work is accomplished. Extend this process until the weight is a pile of sand and we remove one grain at a time, thus raising as much of the weight as high as possible. The piston never gains any kinetic energy because the downward pressure is always very nearly equal to the gas pressure. In other words, the ***maximal useful work*** is obtained by eliminating the ***pressure gradient***.

Would a fluid become "unstirred" if we reversed the direction of stirring? No, that process is irreversible. Similarly, we could easily reverse the piston expansion by adding a grain of sand. Hence ***reversibility*** is the key to ***maximal work***.

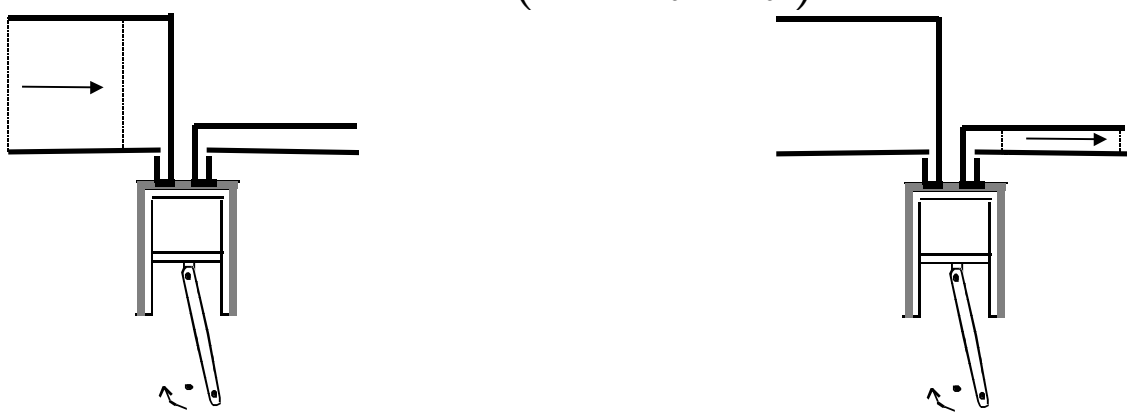
Example 2.8. Energy Balance on a reciprocating compressor

Section 2.7 THE CLOSED SYSTEM PERSPECTIVE (changes in time, *n*=constant)

$$\underline{\dot{Q}} + \underline{\dot{W}}_{EC} + \underline{\dot{W}}_{S} = \frac{d}{dt}\left[n\left(U + \frac{u^2}{2g_c} + \frac{gz}{g_c} \right)\right]$$

$$W_{EC} = (-\int P\, dV)^{\text{beg}\rightarrow\text{mid}} + (-\int P\, dV)^{\text{mid}\rightarrow\text{end}} = -[PV]_{\text{beg}}^{\text{end}} + \int V\, dP$$

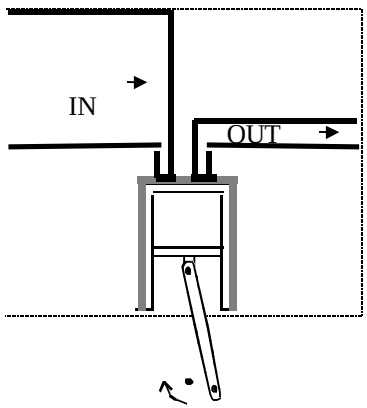
Substitution $\rightarrow$ $$Q - \int PdV = \Delta\left(U + \frac{u^2}{2g_c} + \frac{gz}{g_c} \right) = Q - \Delta(PV) + \int VdP$$



BEFORE AFTER

Energy Balance on a reciprocating compressor(cont.)

Section 2.8. THE STEADY OPEN SYSTEM PERSPECTIVE (changes in space)



A change in perspective does not change the actual energy flows, so copy from previous:

$$\left(U + PV + \frac{u^2}{2g_c} + \frac{gz}{g_c}\right)^{out} - \left(U + PV + \frac{u^2}{2g_c} + \frac{gz}{g_c}\right)^{in} = Q + \int VdP$$

Note the natural appearance of PV energy flows.

For "CONVENIENCE": $U+PV \equiv H$

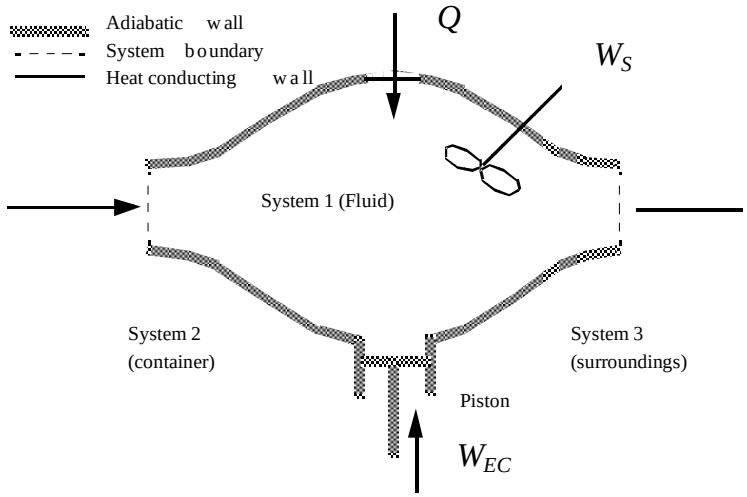
Note: Till now, we have assumed no shaft work going to "stirring" the fluid. This kind of stirring gives rise to internal gradients and frictional losses that make the process "irreversible". Lumping this shaft work with $\int VdP$ form of shaft work gives,

$$\left[H + u^2 / 2 + gz\right]^{out} \dot{m}^{out} dt - \left[H + u^2 / 2 + gz\right]^{in} \dot{m}^{in} dt = \underline{Q} + \underline{W}_S$$

$\dot{m}$ is the magnitude of the mass flow rate, $\underline{Q}$ is the extensive heat, $\underline{W}_S$ is the extensive shaft work.

THE COMPLETE ENERGY BALANCE (changes in space and time)

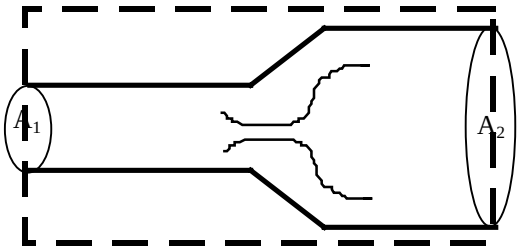
$$\left(H+\frac{u^2}{2g_c}+\frac{gz}{g_c}\right)^{in}\dot{n}^{in}-\left(H+\frac{u^2}{2g_c}+\frac{gz}{g_c}\right)^{out}\dot{n}^{out}+\underline{\dot{Q}}+\underline{\dot{W}}_S+\underline{\dot{W}}_{EC}=\frac{d}{dt}\left[n\left(U+\frac{u^2}{2g_c}+\frac{gz}{g_c}\right)\right]$$



Common Reduced Forms

1. Closed System: $\Delta U = Q + W_{EC}$
2. Open Steady System: $\Delta H = Q + W_S$
3. Open Unsteady System:
   $d(nU) = Hdn$

Example 2.6. Kinetic Energy to Enthalpy



Mass Balance:

$u_1A_1 = u_2A_2 \Rightarrow u_2/u_1 = A_1/A_2 = (D_1/D_2)^2$

Energy Balance:

$Q = 0,\ W = 0,\ \Delta z = 0,\ dU/dt = 0$

$\Rightarrow \Delta H = -\Delta(u^2)/2 = -(u_1^2)/2[(u_2/u_1)^2 - 1] = -(u_1^2)/2\ [(D_1/D_2)^4 - 1]$

$= -6.0^2\ [(D_1/D_2)^4 - 1]/2 = 18\ J/kg$ *when* $D_2 \rightarrow \infty$

$\Delta T = \Delta H/Cp = 18\ J/kg\ /\ 4184\ J/kg\text{-}K = 0.004\ K$

Example 2.10. Continuous adiabatic reversible compression

Suppose 1 kmole/hr of air is adiabatically and reversibly compressed in a continuous process from 5 bars and 298K to 25 bars. Assuming air may be treated as an ideal gas under these conditions, what will be the outlet temperature and the power requirement for the compressor in hp?

Solution:

E-bal: $dH = (Q + W_S)dt = VdP = (RT/P)dP$

$dH = C_P dT = ({}^{RT}/_{P})dP$

Dividing through by T and integrating both sides:

$$\int_{T_1}^{T_2} \frac{C_P dT}{T} = \int_{P_1}^{P_2} \frac{RdP}{P} \Rightarrow C_P \, ln\left(\frac{T_2}{T_1}\right) = R \, ln\left(\frac{P_2}{P_1}\right)$$

Solving for T_2

$$\boxed{\left(\frac{T_2}{T_1}\right) = \left(\frac{P_2}{P_1}\right)^{R/C_P}}$$

This result is encountered extremely often. **<u>Memorize it soon</u>**.

$T_2 = 298(25/5)^{2/7} = 472$ K.

Returning to the E-Bal: $W_S = \Delta H = C_P \Delta T = 8.314*3.5*(472-298) = 5063$ J/mole

Converting to hp: $W_S = 5063$ J/mole*[1000mole/hr]*[1hr/3600s]*[1hp/745.7J/s] = 1.9hp

Example (not in book). Throttles vs. nozzles

A throttle is different from a nozzle in that the throttle makes no attempt to harness the kinetic energy arising from the pressure drop. The energy balance is therefore that much simpler. To illustrate, consider the following situation. Steam at 200 bars and 600°C flows through a valve and out to the atmosphere. What will be the temperature after the expansion?

Solution:

Ebal: $\Delta H=0$

$H(200,600) = 3539$ J/g

$P_2 = 1$ bar

$T_2 = 500 + 50*(3539-3488.7)/(3596.3-3488.7) = 523°C$

Example 2.12 - Heat loss from a turbine

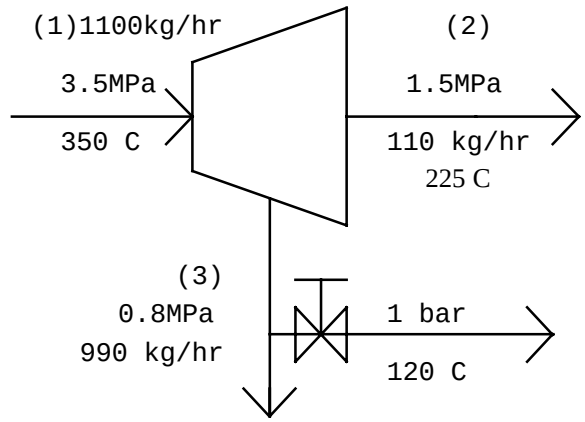
$\underline{W_S}$ = -100kW

Which is right?

$\underline{Q}=\Delta\underline{H} - \underline{W}$

or

$\underline{Q}=\Delta\underline{U} - \underline{W}$?



Note: $H(1.4,225) = [H(1.4,200)+H(1.4,250)]/2 = 2865.5$ kJ/kg

1) $H_1 = H(3.5\text{MPa},350°\text{C}) = 3104.8$ = 3104.8 kJ/kg

2) $H_2 = H(1.5,225) = [H(1.4,225)+H(1.6,225)]/2$ = 2860.0 kJ/kg

3) $H_3 = H(0.8,?)^{\Delta H=0} = H(0.10,120) = 2676.2 + \left(\frac{2776.4 - 2676.2}{150 - 100}\right)20$ = 2716.1 kJ/kg

4) $\Delta\underline{H}$ = 3104.8(1100) - 2860.0(110) - 2716.1(990) = -411,741 kJ/hr

$\underline{Q}=\Delta\underline{H} - \underline{W}$ = -411,741 kJ/hr * 1hr/3600 s - (-100 kJ/s) = -14.4 kW

Example 2.13. Adiabatic expansion of an ideal gas from a leaky tank

Relate the change in temperature to the change in pressure for gas leaking from a tank neglecting the influences of stirring.

Energy Balance:

$$d(nU) = Hdn = ndU + Udn \Rightarrow ndU = (H - U)\, dn$$

$$n = \frac{PV}{RT};\ (H - U) = PV = RT; dU = CvdT; \Rightarrow \frac{PV}{RT} CvdT = RT \quad d\left(\frac{PV}{RT}\right)$$

The volume of the tank is constant, therefore,

$$\frac{C_V}{RT} dT = \frac{T}{P} d\left(\frac{P}{T}\right) = d\ell n\left(P/T\right) \Rightarrow \frac{C_V}{R}\left(\ell n(T_2/T_1)\right) = \ell n\left(P_2/T_2\right) - \ell n\left(P_1/T_1\right)$$

$$C_V\ \ell \mathrm{n}\left(\frac{T_2}{T_1}\right) = R\ell n\left(\frac{P_2 T_1}{P_1 T_2}\right) \Rightarrow \frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{R/(Cv+R)}$$

$$\frac{T_2}{T_1} = \left(P_2/P_1\right)^{(1-1/\gamma)} \qquad \gamma \equiv C_P/C_v\left(= 1.4 \text{ for ideal diatomic gas}\right)$$

Example 2.14. Adiabatically filling a tank with an ideal gas

Helium at 300 K and 3000 bar is fed into an evacuated cylinder until the pressure in the tank is equal to 3000 bar. Calculate the final temperature of the helium in the cylinder (*Cp/R*=5/2)

Solution:

$$n^{in} = \int_{t_i}^{t_f} \dot{n}^{in} dt$$

$$H^{in} n^{in} = \Delta(Un) = U_f n_f = U_f n^{in}$$

$$U_f = H^{in} = U^{in} + PV^{in} = U^{in} + RT^{in}$$

$$\Delta U = Cv(T_f - T^{in}) = RT^{in} \Rightarrow T_f = T^{in}(R + Cv)/Cv = T^{in} Cp/Cv$$

Example 2.15. Adiabatic expansion of steam from a leaky tank

An insulated tank initially contains 500 kg of steam and water at 2.0 MPa. Half of the tank volume is occupied by liquid and half by vapor. 25 kg of moisture free vapor is vented from the tank so that the pressure and temperature are always uniform throughout the tank. Analyze the situation carefully and calculate the final pressure in the tank.

Solution:

$$E-bal: \quad \int H^{out}\dot{m}^{out}dt = \Delta(mU)$$

Trick: note that H^{out} is the enthalpy of the saturated vapor which is 2795±5 J/g over a wide range of pressures near 2.0MPa. Therefore assume constant and factor.

$$\Delta(Um) = H^{out}\int \dot{m}^{out}dt = H^{out}\Delta m$$

$$\Rightarrow \Delta(Um) = -2795(25) = -69{,}875kJ$$

$$U_i = q*2600.3+(1-q)906.44$$

$$V_i = q*0.09963+(1-q)0.001177$$

$$But\ m_i = 500\,kg = \frac{\underline{V}_T}{2}\left[\frac{1}{0.0947}+\frac{1}{0.001181}\right] \Rightarrow \underline{V}_T = 1.166\,m^3$$

$\Rightarrow V_i$ = 1.166 m^3/500 kg = 0.00233 $\Rightarrow q_i$ = 0.0123 $\Rightarrow U_i$ = 938.7 kJ/kg

E-Bal $\Rightarrow U_f$ (475) – 500(938.7) = -69875 $\Rightarrow U_f$ = 841.0 kJ/kg

Procedure:

(1) Guess T_f,

(2) get P from V_f = 1.166/475=0.00245

(3) get U_f

(4) if U_f = 841.0 stop, otherwise go to (1)

Calculations:

P_f	T_f°C	V^L	V^V	U^L	ΔU^{vap}	q	U_f
2.106	215	0.001181	0.0947	918.04	1681.9	0.0123	938.7
1.3988	195	0.01149	0.1409	828.18	1763.6	0.0093	845

Close Enough!

P2.16 Steam at 150 bars and 600 C passes through a heater expander…

Steam at 150 bars and 600 C passes through a heater expander and emerges at 100 bars and 700 C. There is no flow of work into or out of the heater-expander, but heat is supplied.

a) Using the steam tables, compute the flow of heat into the heater expander per mole of steam.

b) Compute the value of [H(150,600)-H(1,600)]/RT for steam at the inlet conditions, where H is on a molar basis.

E-bal: $Q=\Delta H$

a) ΔH= H(700C,10MPa)-H(600C,15MPa) = 3840-3582 = 258 J/g

b) H(600C,15MPa) - H(600C,0.1MPa) = 3582- 3705 = -123J/g

$$\frac{H-H^{ig}}{RT}=\frac{-122.4*18}{8.314*873}=-0.3035$$

When we come to Chapter 7, we reverse this procedure. That is, we will estimate (H-H^{ig}) then construct "steam tables" based on those estimates. We will also construct "freon tables," "butane tables," and show how to construct thermodynamic property tables for any other compound that you may encounter.

Example (not in book). One stroke of an old-fashioned steam engine

In an old-fashioned locomotive an insulated piston+cylinder is connected through a valve to a steam supply line at 3 MPa and 300°C. The back side of the piston is vented to the atmosphere at the right side of the cylinder. The volume of the cylinder is 70 liters. When the valve opens the piston is touching the left side of the cylinder. As the piston moves to the right it accomplishes 108 kJ of work before it touches the right side of the cylinder. Then, the cylinder contains 0.5 kg of steam. What is the final pressure of steam in the cylinder? (Do not assume frictionless)

Solution:

E-bal: $\Delta U = m^{in}H^{in} + Q + W$ for piston+cylinder as the system (ΔH=0 across valve)

V_f = 0.070/0.5 =0.14 m^3/kg; $U_f = H(3{,}300) + 0 - 108\text{kJ}/0.5\text{kg} = 2993 - 216 = 2777$ kJ/kg

Referring to the steam tables, we see that these conditions are satisfied at 1.8 MPa. T=300°C.